Sorption and Diffusion Studies of Pu(IV) and Pu(IV)-EDTA onto and through Hanford Soil

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Summary

Widely present in the mixed wastes at the Hanford site, ethylenediametetraacetic acid (EDTA) can solubilize radionuclides such as plutonium and may increase their mobility in the environment. In the present study, we evaluated the effect of EDTA on the migration of Pu(IV) at the Hanford site through laboratory-based sorption and diffusion experiments at ambient temperature and atmosphere. The sorption ratio, R%, was determined as a function of pH, EDTA concentration, and solid-liquid ratio. At a plutonium concentration of $5x10^{-5}$ M in the presence of EDTA ($> 10^{-3}$M), the Pu(IV) sorption ratio decreased significantly. The effective diffusion coefficient, D_e, was estimated at 3.54×10^{-6} cm^2/sec for Pu(IV)-EDTA at pH=5.5.

Introduction

Plutonium production at U.S. Department of Energy Hanford site has created massive amounts of radioactive and mixed wastes. Over 1.3 trillion liters of liquid waste have been discharged into the ground, the largest part of which has been absorbed by the upper soil layers with a small fraction migrating into the groundwater. Approximately

350 million liters of other low and high-level mixed wastes were stored in underground tanks between 1944 and 1980 [1]. These tanks contain organic materials that were introduced during the production and processing of plutonium, such as ethylenediametetraacetic acid (EDTA), tributyl phosphate, hexone, paraffin hydrocarbon and other minor organic and inorganic components. The quantity of EDTA is estimated to be 83 metric tons in the underground tanks [2]. Several single-shell tanks are known or suspected to have leaked. It was reported that since 1995, approximately four million liters of mixed waste might have entered the soil beneath the single-shell tanks. This volume of waste is estimated to contain as much as one million curies of radioactivity [1].

EDTA in the mixed waste may form stable and soluble complexes with radionuclides and heavy metals (e.g., plutonium, americium, neptunium, cobalt and iron). Pu(IV)-EDTA is one of the most stable of these complexes [3], and its presence in the mixed waste may promote the migration of Pu in the subsurface and groundwaters.

Several studies have been performed to understand the effect of EDTA on the mobility of heavy metals such as Ca, Mg, Ni, Co, Cu, Zn, Cd and Fe in river sediment/water systems [4-6]. These studies showed that EDTA can alter the solubility and sorption of these metals in the environment under certain conditions (pH, EDTA and electrolytes concentrations).

The complexation of Pu(IV) with EDTA has been previously studied and reported by several authors. Cauchetier and Foreman determined complexation constants of $10^{25.6}$ and $1.26 \times 10^{17.10}$, respectively, for the 1:1 Pu(IV)-EDTA complex [7-8]. Chopin and Rai have studied EDTA complexation with tetravalent actinides and found formation constants generally higher than 10^{24} for the 1:1 An(IV)-EDTA complexes [9]. Al

Mahamid et al. studied the complexation behavior of plutonium in several oxidation states in the presence of EDTA at pH 5 and 8. They found that Pu(III) was oxidized and Pu(V) and Pu(VI) were reduced either partially or completely to the Pu(IV)-EDTA complex [10]. Reed et al. have investigated the complexation of Pu(VI) by EDTA at low and high ionic strength and have observed reduction of Pu(VI) to Pu(IV)-EDTA [11].

There are limited data concerning the influence of EDTA on actinide sorption at mineral surfaces. Weiss and Colombo studied the sorption of Am(III) by shale, montmorillonite, kaolinite, illite, limonite and vermiculite. In most cases, the sorption in presence of 100 ppm of EDTA was much lower than for the same systems containing no EDTA. The presence of EDTA decreased K_d values by one order of magnitude for Am-vermiculite and by seven orders of magnitude for the Am-kaolinite system [12]. Al Mahamid and Hakem have studied the biosorption of Pu(III) and Pu(IV)-EDTA on microbes that are known to have a high sorption capacity, such as *Pseudomonas Aeroginosas* and *Mycobacterium Parafortutium*. It was found that the presence of EDTA drastically reduced the K_d values in these systems [13,14].

The results of these studies suggest that EDTA can affect the migration of Pu(IV) through the formation of stable complexes which compete with the corresponding sorption processes. In the present paper, we performed several laboratory experiments to understand the impact of EDTA on the migration of plutonium at the Hanford site. We studied the sorption and the diffusion of Pu(IV) and Pu(IV)-EDTA onto and through Hanford soil. Sorption experiments were investigated as a function of pH, soil-liquid ratio, (m/V), and EDTA concentration. The diffusion study was performed by the steady state (through-diffusion) method using diaphragm cells for both Pu(IV) and Pu(IV)-

EDTA. This method was largely used by McKinley and Swaminathan [15], Skagius and

Neretnieks [16], and Hakem et al. [17] for the study of the diffusion of sorbing elements

such as cesium, strontium and nonsorbing elements such as iodine and tritium.

Experimental

Reagents

The reagents used in our experiments were 1 M NaOH, 1M HCL (Baker), 10^{-1} M Na_2H_2EDTA (Fisher),

and Ecolite liquid scintillator cocktail (ICN Biomededicals). All solutions were prepared using fresh

deionized, distilled water. Plutonium with a mass composition of 79% Pu-239, 18% Pu-240 and 3% Pu-

238 provided by Lawrence Livermore National Laboratory was used. A 10^{-3} M Pu(IV) stock solution was

prepared by electrochemical technique in 1M HCl. A second stock solution was prepared containing 10^{-3}

M Pu(IV) in 10^{-1} M EDTA. The purity of the oxidation state was verified by UV spectrophotometry.

Soil Characterization

The soil used in the experiments was recovered from the 200 East Area at the Hanford site. Samples were

collected from 0 to 0.3 m depth. Soil characterization has been previously performed and published [18].

The dominant minerals in the total sediment sample (<2 mm) were quartz and plagioclase, the major

mineral in the <2 μm fraction was smectite. The pH and CEC of the soil are 8.2 and 6.0 meq/100g

respectively.

Apparatus and Methods

A Cary 500 Scan (Varian) UV-Vis-NIR spectrophotometer with the Cary WindUV software was used to

determine the oxidation state and the concentrations of the Pu(IV) and Pu(IV)-EDTA stock solutions.

A Tri-Carb[R](Packard) Liquid Scintillator Analyser was used to measure the plutonium activity.

pH measurements were performed using a semimicro Ross combination pH glass electrode (Orion

Research Inc.). The electrode was calibrated with NIST-traceable standard buffer solutions (pH 4 and 7).

Sorption Experiments

All experiments were performed by static batch method at room temperature under normal atmosphere.

Experiments were carried out as a function of pH, soil-liquid ratio (m/V), and EDTA concentration. The

samples were prepared by mixing a given amount of soil with an amount of the Pu(IV) stock solution in the presence or in the absence of EDTA. The final Pu concentration for all samples was 5×10^{-5} M. The pH was adjusted by adding a few μL of 0.1 M HCL or NaOH. For the sorption experiments conducted in the presence of EDTA, formation of the Pu(IV)-EDTA complex was checked by UV spectrophotometry after two days. For each set of sorption experiments, a second series of "control" solutions were prepared in the absence of soil. These samples were used to monitor any precipitation or sorption of plutonium onto the container walls during the experiments. All solutions were kept in closed polyethylene containers and were gently shaken for one week on an Environ-Shaker (Lab-Line Instrument, Inc.) with a slow and stable shaking speed. Separation of the soil from the liquid was performed by ultrafiltration using Centricon-30 filters, 4.1 nm pore size (Amicon). Ultrafiltration eliminated potential problems caused by the presence of colloids or pseudo-colloids in the supernatant. Colloidal particles have very high surface specific areas and can distort measurements because of strong plutonium sorption. Pu(IV) and Pu(IV)-EDTA sorption was

evaluated using the sorption ratio, R%, described in equation (1): $R\% = \dfrac{[Ac]_0 - [Ac]_{sol}}{[Ac]_0} \times 100$ (1)

where $[Ac]_0$ = Pu(IV) or Pu(IV)-EDTA initial concentration and $[Ac]_{sol}$ = Pu(IV) or Pu(IV)-EDTA concentration in solution after filtration.

XANES Data Acquisition

X-ray absorption near-edge structure (XANES) spectroscopy was used to determine the oxidation state of Pu in the dilute control solutions and the Pu sorbed onto soil. XANES measurements were performed on selected samples at the Stanford Synchrotron Radiation Laboratory (SSRL). Plutonium L_{II}-edge XANES spectra were measured on wiggler beamline 4-1 under normal ring operating conditions (3.0 GeV, 50-100 mA). Energy scans were obtained using a Si (220) double-crystal monochromator and a vertical slit width of 0.5 mm. The higher order harmonic content of the beam was rejected by detuning the crystals in the monochromator so that the incident flux was reduced to 50% of its maximum. All samples were measured in fluorescence mode using a Ge solid state detector developed at Lawrence Berkeley National Laboratory. XANES data reduction and normalization was done using the suite of programs EXAFSPAK developed by G. George at SSRL. Typically, 7 XANES scans were collected from each sample and the results averaged.

The spectra were energy calibrated by simultaneously measuring the absorption spectrum for the reference sample PuO_2, and setting the energy of the first inflection point, E_r, at 22258.0 eV.

Diffusion

The diffusion studies were performed by the steady state method using diaphragm cells. According to Lever [19], the steady state method gives the best estimate for the effective diffusion coefficient, D_e. The characteristics of the cells used in the present work are listed in Table 1. Details of the cell can be found in McKinley and Swaminathan [15]. In each cell, a sample of Pu-free Hanford soil (25 g), was sandwiched between two reservoirs. Initially, the upstream reservoir contained $5x10^{-5}$ M Pu(IV) in $2x10^{-1}$ M EDTA solution at pH 5.5 ± 0.5, and the second reservoir contained deionised-distilled water. An identical set of experiments was carried out in the absence of EDTA. As the plutonium diffused through the soil, the concentrations in both reservoirs were monitored as a function of time. In order to ensure homogeneity of the solutions in the cells, they were stirred immediately prior to assay. We periodically removed 1 mL of the solution from the upstream and from the downstream reservoirs, and measured the respective Pu concentrations by liquid scintillation.

Results and Interpretation

Speciation of Pu(IV) and Pu(IV)-EDTA

Using Mineql$^+$, a chemical program originated by J. C. Westal, we performed the speciation of Pu(IV) and Pu(IV)-EDTA as a function of pH and EDTA concentrations. The hydrolysis and complexation constants used are reported in Table 2 [20-21]. The Pu(IV) and Pu(IV)-EDTA speciations are reported in Figures 1-a and 1-b. In the absence of complexing agents and for 5<pH<8, $Pu(OH)_4$ and $Pu(OH)_5^-$ are the major species present in the solution. In the presence of 0.1 M of EDTA, Pu(IV)-EDTA is the major species at pH<6, $Pu(OH)_5^-$ is the major species at pH>8. For pH ranged from 6 to 8, both species Pu(IV)-EDTA and $Pu(OH)_5^-$ are present.

XANES Spectroscopy

The Pu oxidation state in selected samples was evaluated using XANES spectroscopy. Figure 2 shows the normalized Pu L_{II}-edge XANES spectra for: a) 0.2 mM Pu(IV)-EDTA complex solution at pH 4; b) ~ 20 μg Pu(IV) sorbed onto 12 mg Hanford soil at pH 4; and c) ~20 μg Pu(IV) sorbed onto 100 mg Hanford soil in the presence of 100 μM EDTA at pH 4. For comparison purposes, the XANES spectra for the reference aquo species An^{3+}, An^{4+}, AnO_2^+, and AnO_2^{2+} (where An = U, Np, or Pu) are also shown [22]. In this case, the reference spectra demonstrate specific spectral features (i.e., absorption peak maxima and positions) which serve as signatures for the different actinide oxidation states. The results shown in Figure 2 demonstrate that the Pu in the Hanford soil and/or EDTA samples is present (>90%) in the tetravalent, Pu(IV), oxidation state.

Effect of pH on Sorption

We have studied the effect of pH on the Pu(IV) sorption for an initial concentration of Pu(IV)=5×10^{-5} M and a solid-liquid ratio 0.05 g/mL. An inspection of the results in Table 3 indicates that the Pu(IV) sorption is very high, and increases from 50% to 96.7% over the pH range from 4 to 9.2. In this pH range, Pu(IV) hydrolysis is very high and $Pu(OH)_4$ and $Pu(OH)_5^-$ are the major species (Figure 2-a). The sorption can be explained as occurring through physiosorption where even neutral or negatively charged plutonium species are strongly sorbed onto the surface of the soil particles [23].

Effect of solid-liquid ratio (m/V)

The dependence of plutonium sorption on the sorbent mass was investigated. The solid-liquid ratio (m/V) was varied from 0.0045 to 0.244 g/mL and from 0.006 to 0.1355 g/mL for Pu(IV)-EDTA and Pu(IV), respectively. The initial Pu concentration was 5×10^{-5} M in

the presence or in the absence of 0.1 M EDTA. The pH of the solutions was 6.0±0.5. The results are shown in Figure 3. The sorption of Pu(IV) increases rapidly with increasing m/V ratios. The Pu(IV) sorption ratio reached 98.81% for an m/V ratio greater than 0.1355 g/mL. This is due mainly to the availability of more adsorption/exchange sites with greater amount of soil. However, the sorption of Pu(IV)-EDTA was slightly dependent on the m/V ratio and never exceeded 13%.

Effect of EDTA concentration

The effect of EDTA in the sorption of Pu(IV) onto Hanford soil was studied at pH 5.0±0.5 by varying the concentration of EDTA from 10^{-5} to 10^{-1} M. The initial concentration of plutonium was 5×10^{-5} M, and the soil m/V ratio was 0.02 g/mL. Table 4 shows that at low concentrations (10^{-5} to 10^{-3} M), EDTA did not affect the plutonium sorption which remained very high (>95%). However, at higher EDTA concentrations (10^{-3} to 10^{-1} M), the sorption of plutonium decreased significantly. One explanation for this effect is that increasing the amount of EDTA caused the Pu-EDTA complex formation to dominate over the Pu sorption on the soil. Another possibility is that the excess of EDTA in the solution can compete with plutonium for sorption sites on the soil. Given the speciation expected at pH 5, this latter scenario could involve competition between species such as $EDTA^{2-}$ and $Pu(OH)_5^-$ or $Pu(OH)_4$. These results suggest that in Hanford soil at pH 5, EDTA must be present in significant excess in order to alter Pu sorption and subsequent migration.

Diffusion Study

Since the Pu concentration in the upstream reservoir decreases as a function of time, the total Pu concentration at any instant is given by: $C_0 = C_{up} + C_{dw} + C_{sp}$ (2)

8

C_0 is the initial total Pu concentration, C_{up} and C_{dw} are the Pu concentrations in the upstream and the downstream reservoirs, respectively, C_{sp} is the Pu concentration sorbed in the soil. Figure 4-a and 4-b represent the variations of the ratio C_{dw}/C_{up} and the sorption ratio, R%, respectively, as a function of time for Pu(IV) and Pu(IV)-EDTA. Pu(IV) diffusion breakthrough did not occur even after 128 days. Pu(IV) was not detected in the downstream reservoir, and the sorption on the soil reached 99.6% after 128 days. In the case of Pu(IV)-EDTA diffusion, the sorption onto the soil was very low and never exceeded 2%, and its diffusion was relatively fast. The ratio C_{dw}/C_{up} reached 0.12, 0.23, 0.5, and 0.79 after 8, 16, 51 and 128 days, respectively. As one can see in Figure 4-a, C_{dw}/C_{up} increased steadily. After a long time, the concentrations in the two reservoirs (upstream and downstream) equilibrate and the ratio C_{dw}/C_{up} slowly approaches unity.

In order to estimate the diffusion coefficient for Pu(IV)-EDTA, we used Fick's second law modified for porous media by introducing the effective diffusion coefficient D_e and the rock capacity factor α [19]:

$$D_e \frac{\partial^2 C}{\partial X^2} = \alpha \frac{\partial C}{\partial t} \qquad (3)$$

No analytical solutions to equation (3) are currently available under the conditions of our diffusion cell experiments (i.e. finite liquid volume and temporally variable concentrations in the upstream and downstream reservoirs) [24]. However, we assume that for a short time study (<11 days), the volume of the downstream reservoir is constant and the C_{up} is high enough to be constant and equal to C_0. Then, the derivation of equation (3) given by Lever [19] is:

$$\frac{C_{dw} V}{A l C_0} = \frac{D_e t}{l^2} - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{D_e n^2 \pi^2 t}{l^2 \alpha}\right) \qquad (4)$$

9

Where V is the volume of the downstream cell, A and l are respectively the cross sectional area and thickness of the soil sample. At long times, the exponential term falls away to zero, so the equation (4) can be simplified to $C_{dw} = C_0 \left(\dfrac{AD_e}{Vl} t - \dfrac{Al\alpha}{6V} \right)$ (5).

From the slope of the equation (5), we estimated D_e for Pu(IV)-EDTA diffusion equal to 3.54×10^{-6} cm^2/s.

Conclusions

Sorption and diffusion experiments were carried out to investigate the effect of EDTA on the migration of plutonium through Hanford soil. It was found that Pu(IV) is highly sorbed by the soil and did not diffuse through it. The presence of EDTA at high concentrations ($>10^{-3}$ M) in 5×10^{-5} M Pu(IV) solutions decreased the sorption significantly. This may be explained in that the excess of EDTA can promote complexation or sorb onto the soil leaving less sites available for Pu. At low concentrations ($<10^{-3}$ M), EDTA did not influence the sorption of Pu. These results indicate that in Hanford soil at pH 5, EDTA must be present in a significant excess in order to alter Pu sorption and subsequent migration. Pu(IV) at 5×10^{-5} M in the presence of EDTA at 10^{-1} M diffused through Hanford soil very rapidly, and D_e was estimated to 3.54×10^{-6} cm^2/s. We did not detect any diffusion of Pu(IV) even after 128 days due to high sorption onto the soil.

Acknowledgements

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Table 1. Diffusion Cell Characteristics

Parameters	Dimensions
Volume of upstream cell	500 cm^3
Volume of downstream cell	500 cm^3
Cell diameter	5 cm
Thickness of the soil material	1 cm
Thickness of metal disc	0.156 cm
Porosity of metal disc	40 %
Particle size of metal disc	20 μm

Table 2. Hydrolysis and Complexation Constants for Pu(IV)

Reactions	Log K	I (M)	References
$Pu^{4+} + H_2O \text{------------}> Pu(OH)^{3+}$	-0.3	0	(a)
$Pu^{4+} + 2\ H_2O \text{----------}> Pu(OH)_2^{2+}$	-2.3	0	(a)
$Pu^{4+} + 3\ H_2O \text{----------}> Pu(OH)_3^{+}$	-5.3	0	(a)
$Pu^{4+} + 4\ H_2O \text{----------}> Pu(OH)_4$	-9.5	0	(a)
$Pu^{4+} + 5\ H_2O \text{----------}> Pu(OH)_5^{-}$	-15	0	(a)
$Pu^{4+} + H_4EDTA \text{------}> PuEDTA + 4H^{+}$	26.14	1	(b)

[a] Reference [15], [b] Reference [16]

Table 3. Effect of pH on Pu(IV) Sorption

pH	R%
4	50
6.76	87.83
7.01	96.74
8.24	96.6
9.23	91

Table 4. Effect of EDTA on Pu(IV) Sorption

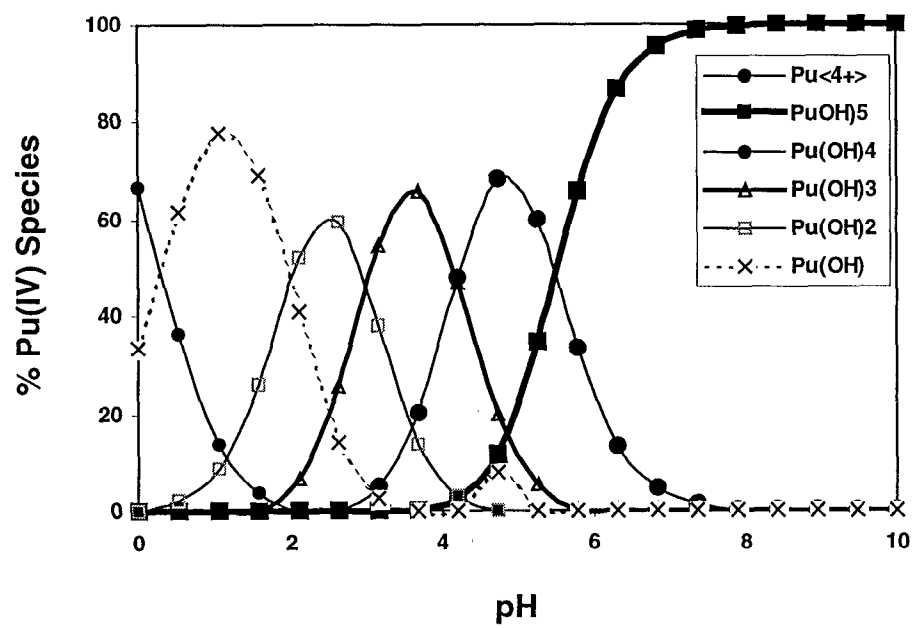| [EDTA], M	R%
0.1	0
0.01	0
0.001	95.24631
0.0001	99.63982
0.00001	99.78725

Fig. 1a. Pu(IV) Speciation as a Function of pH
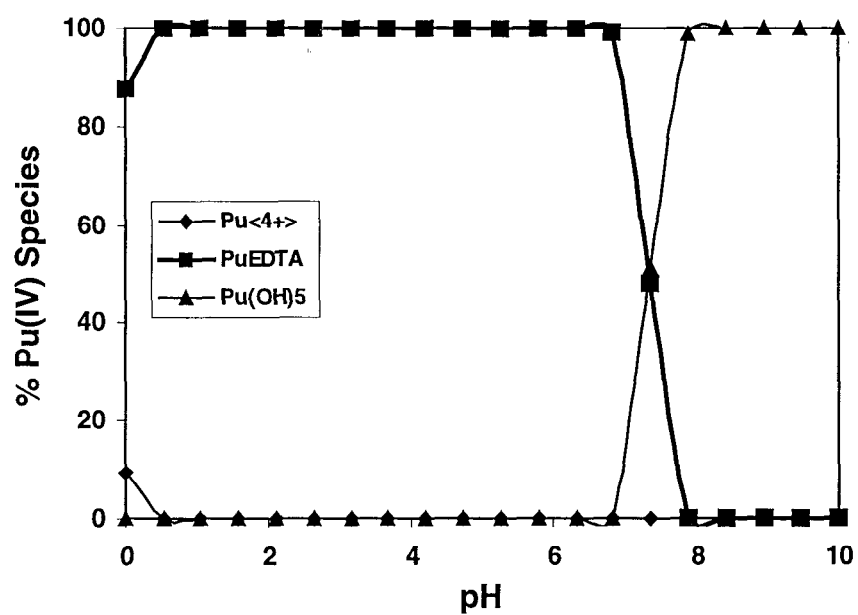
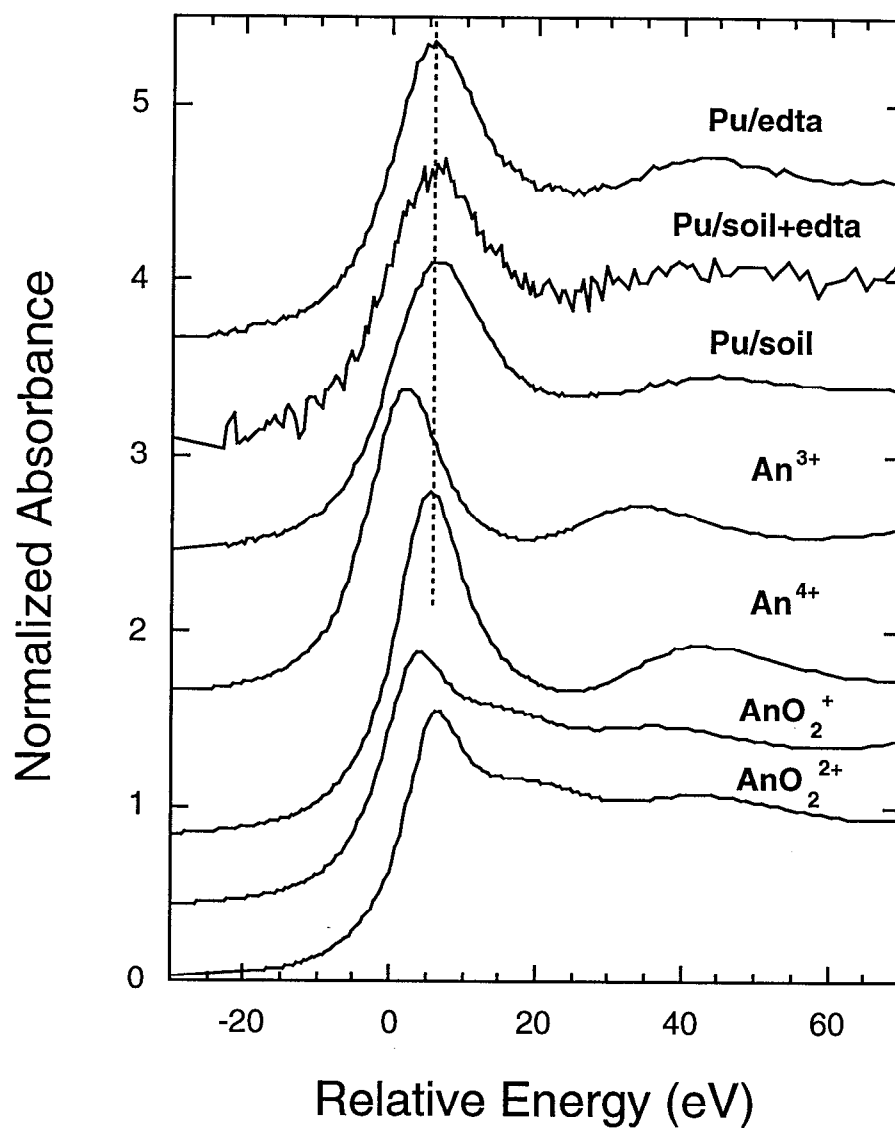**Fig. 1b.** Pu(IV)-EDTA Complexation, Pu(IV)=5x10^{-5} M and [EDTA]=10^{-1} M

Fig 2. Pu L_{III}-Edge XANES Spectra of Pu(IV) in the Presence of Hanford Soil and EDTA Complexing Agent. A Comparison with the XANES Spectra for the Reference Aquo Species An^{3+}, An^{4+}, AnO_2^{+}, and AnO_2^{2+} (Where An = U, Np, Or Pu) Shows that the Pu is Present in the Tetravalent Oxidation State.
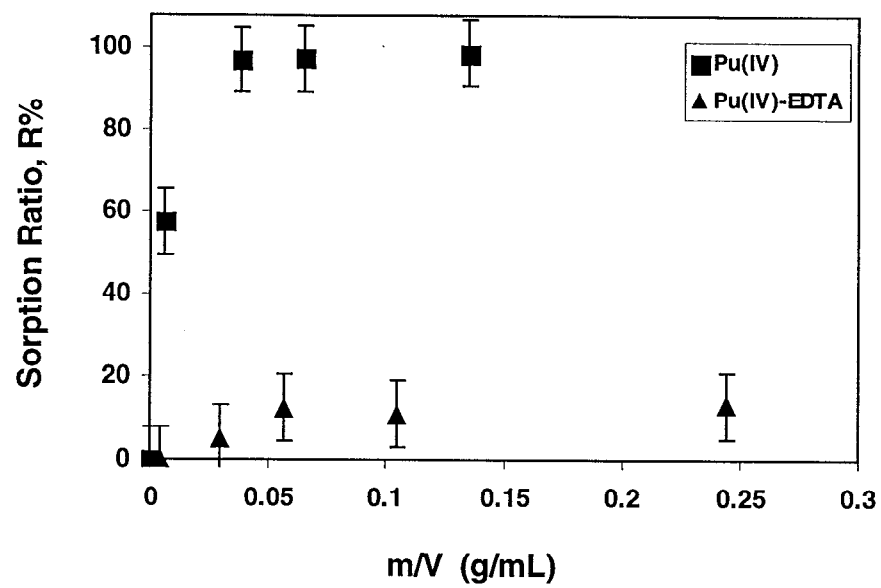
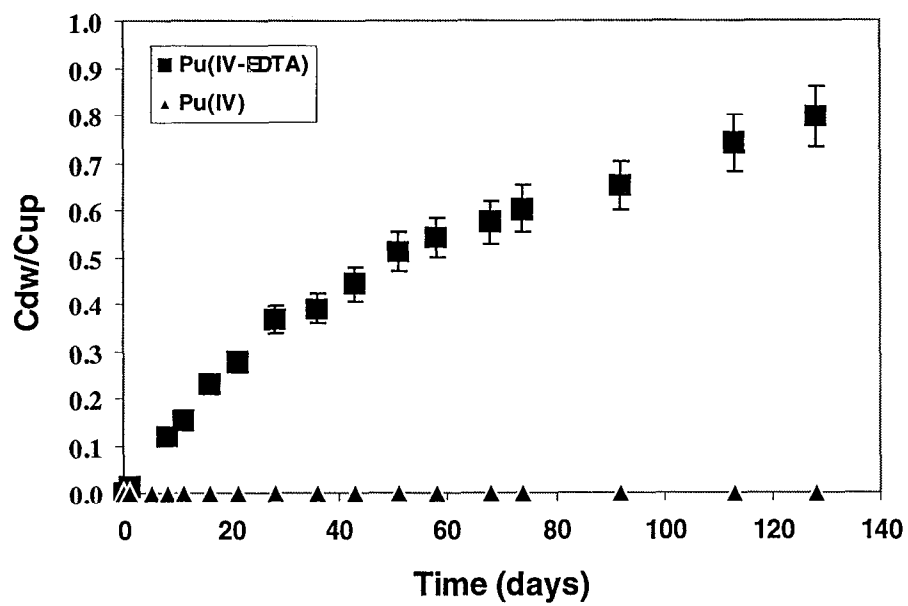**Fig. 3.** Sorption of Pu(IV) and Pu(IV)-EDTA as a Function of m/V

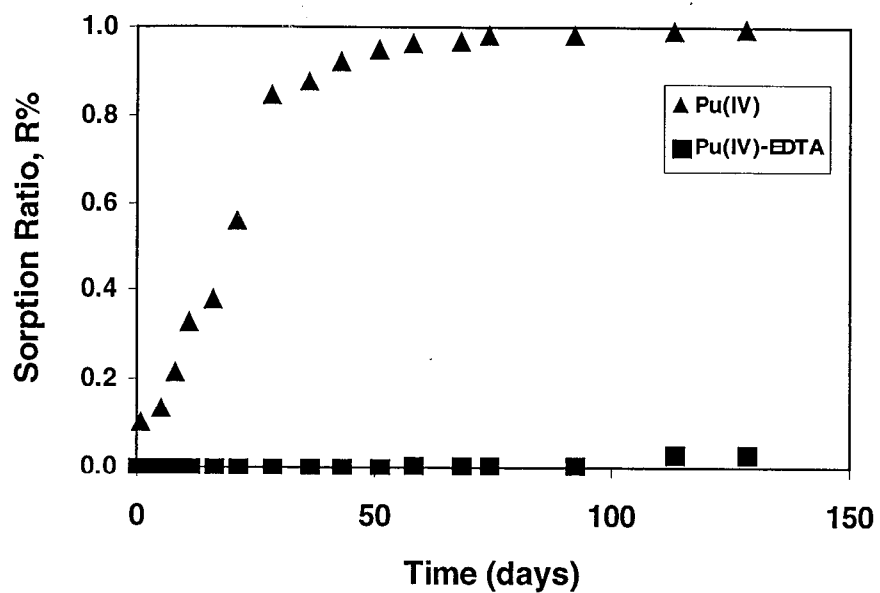**Fig. 4-a.** Diffusion of Pu(IV) and Pu(IV)-EDTA through Hanford Soil

Fig. 4b. Sorption of Pu(IV) and Pu(IV) during the Diffusion Study